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A DIGLYME ADDUCT OF TIN(IV) CHLORIDE FORMED ON DRYING AROMATIC —ETC(U)

AUG 80 W A GUSTAVSON, J J ZUCKERMAN

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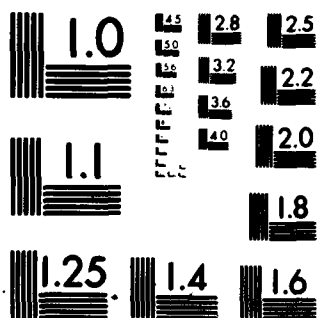
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A DIGLYME ADDUCT OF TIN(IV) CHLORIDE  
FORMED ON DRYING AROMATIC SOLVENTS BY THE  
BENZOPHENONE KETYL/POTASSIUM METAL METHOD

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ABSTRACT

Use of diglyme (diethyleneglycoldimethylether) for solubilization in the benzophenone ketyl/potassium metal method for drying and deoxygenating aromatic solvents can result in contamination of the distilled solvent with subsequent formation of adducts with Lewis acids. The diglyme adduct of tin(IV) chloride is isolated, and the magnitude of its tin-119m Mössbauer Quadrupole Splitting interpreted in terms of its structure.

INTRODUCTION

An excellent method for the removal of water and oxygen from aromatic solvents is distillation from potassium metal. A popular procedure is to add benzophenone to the solvent flask and to allow the mixture to reflux under dry nitrogen or argon until the purple color of the resulting ketyl, indicative of the absence of water, persists.<sup>1,2</sup> One problem that is often encountered is the insolubility of the ketyl in some common aromatic solvents. This problem can be solved by the addition of small amounts of diglyme [diethylene-

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glycolmethylether, bis(2-methoxyethyl)ether] to the solvent flask.<sup>3</sup>

#### RESULTS AND DISCUSSION

During the synthesis of tetrakis(cyclopentadienyl)tin(IV) and dicyclopentadienyltin dichloride, tin(IV) chloride solutions of benzene (a suspected carcinogen) or toluene are added to lithium cyclopentadiene and tetrakis(cyclopentadienyl)tin(IV), respectively.<sup>4</sup> It was noted that addition under nitrogen of freshly distilled tin(IV) chloride to benzene or toluene freshly distilled from potassium and the benzophenone ketyl to which diglyme had been added resulted in the formation of a green-black colored oil. The formation of such an oil by this sequence has not been previously noted. The oil could be filtered by gravity under nitrogen, and was dried in vacuo for two hours. Upon drying the material changed to a light grey colored solid, which became an oil again when exposed to the atmosphere.

The amount of solid isolated was quite small (1.3 g obtained from 11.2 g  $\text{SnCl}_4$ ), but the results were reproducible, and the dried solid melted at 120-123°C (decomp.) whether from benzene or toluene.

The infrared spectra (Nujol and halocarbon mulls and CsI plates) contained prominent bands at 2955(s), 1445(s), 1279(s), 1246(m), 1193(s), 1119(m), 1008(m), 923(s), 904(s), 826(m), 786(m), 322(w), and a very broad band at  $2020\text{ cm}^{-1}$ .

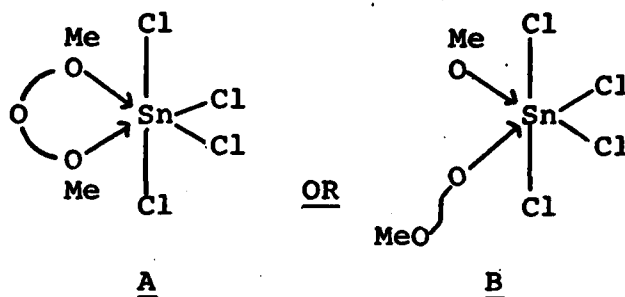
The tin-119m Mössbauer spectrum contained a doublet with Isomer Shift (I.S.) =  $0.49 \pm 0.01$  and Quadrupole Splitting (Q.S.) =  $1.10 \pm 0.02\text{ mm/s}$ , thus indicating that very electronegative elements are bonded to tin, and that the tin atom has a coordination number greater than four ( $\rho = \text{Q.S.}/\text{I.S.} = 2.25$ ;  $\tau = 1.05 \pm 0.03\text{ mm/s}$ ).<sup>5</sup>

The mass spectrum was identical with that of  $\text{SnCl}_4$ , with no peaks higher than  $M/e = 263$  (calculated  $M/e = 259$  for  $^{119}\text{Sn}$ ). Weak fragments at  $m/e = 59$  (9.8%), 77 (1.5%) and 89 (9.4%) can be attributed to diglyme itself.

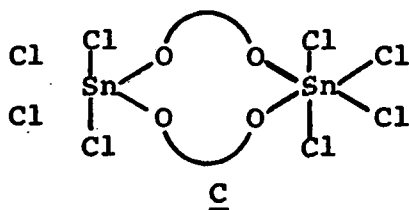
The analytical data for the material are: Found: C, 17.34; H, 3.29; O, 12.50; Sn, 31.98; Cl, 35.29%. These data correspond to an empirical formula of  $\text{SnCl}_4 \cdot \text{C}_6\text{H}_{14}\text{O}_3$  (Calculated: C, 18.26; H, 3.58; O, 12.16; Sn, 30.07; Cl, 35.93%). This is the empirical formula of a 1:1 complex between tin(IV) chloride and diglyme. The data given above are also consistent with this formulation, and an identical product was obtained by mixing diglyme and tin(IV) chloride neat.

The infrared absorption at  $322\text{ cm}^{-1}$  can be assigned to the  $\nu(\text{Sn}-\text{Cl})$  stretching modes, but the position of the  $\nu(\text{Sn}=\text{O})$  in the chelated adduct cannot be determined with confidence.<sup>6</sup>

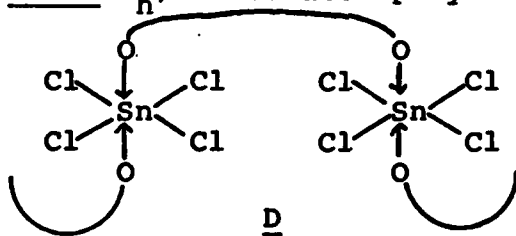
Tin-119m Mössbauer quadrupole splittings are generally unresolvable for  $\text{SnCl}_4\text{B}_2$  systems with cis- $\text{O}_h$  ( $\text{C}_{2v}$ ) symmetries, where the donor atom in the ligand B is oxygen, nitrogen, phosphorus or arsenic.<sup>7</sup> Trans- $\text{O}_h$  ( $\text{D}_{4h}$ ) complexes in which the donor atom in the ligand B is oxygen give rise to Q.S. values of 0.83-1.57 mm/s, but the oxygen is double-bonded to carbon, phosphorus or sulfur in each case studied.<sup>7,8</sup> Mössbauer data for the  $\text{SnCl}_4$  complex of 1,2-dimethoxyethane, an aliphatic diether capable of engaging in chelation, show a small splitting (I.S. = 0.51; Q.S. = 0.80).<sup>9</sup> A monomeric molecular complex of the expected cis- $\text{O}_h$  structures:



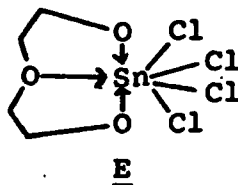
should give rise to a singlet resonance in the Mössbauer spectrum. Point charge calculations predict that the  $\text{SnCl}_4\text{B}_2$  geometry about each tin atom in the less likely dimer:



should give rise to a Q.S. value equal to that given by the cis- $\text{O}_h$   $\text{SnCl}_4\text{B}_2$  arrangement<sup>10,11</sup> which is unresolvable. Only a trans- $\text{O}_h$ , associated polymeric structure such as:



would seem to satisfy the requirements of the observed Q.S. value of 1.10 mm/s, unless it can be argued that the distortion wrought by the aliphatic ether oxygen-tin linkage is greater than that brought about by carbonyl or other double-bonded  $\text{P}=\text{O}$ ,  $\text{As}=\text{O}$ , or  $\text{S}=\text{O}$  coordination. Another, even less likely possibility, is a seven-coordinated structure:



A diglyme adduct of tin(IV) chloride was reported in the late 1960's by Gol'dshtein, et al.,<sup>12,13</sup> but while the authors reported the dipole moment ( $\mu = 8.15$  D), heat of formation ( $\Delta H = -20$  Kcal/mole), and dielectric titration curves, no spectroscopic data or physical properties were given. To our knowledge, this is the first time that this adduct has been isolated and characterized.

The use of diglyme for ketal solubilization must be followed by its careful removal in order to avoid small amounts of diglyme from distilling with the solvent, and forming adducts with Lewis acids in subsequent solvent use.

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